

Flame Retardancy Behaviors and Structural Properties of Polypropylene/Nano-SiO₂ Composite Textile Filaments

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ABSTRACT: The number of efforts about modifying the properties of polymeric fibers by organic or inorganic particles has increased recently because of high-tech applications of textiles. In addition to these attempts, the discovery of nanotechnology also leads to the development of nanoparticles for various end uses such as nanocomposite fibers. In this article, we aimed to produce slow burning or flame retardant polypropylene filaments for carpet pile yarns by incorporating SiO₂ nanoparticles into polymer. Therefore, we present the preparation of filaments incorporating 0.3, 1, and 3% SiO₂ nanoparticles and investigate the effects of nanoparticles on the flame retardancy and structural behavior of filaments. Polypropylene and nanoparticles were compounded by melt-compound-

ing using twin-screw extruder before spinning. Filaments with trilobal cross sections were spun using pilot melt spinning equipment. The structural properties of nanocomposite fibers were analyzed using X-ray diffractometry, differential scanning calorimetry, scanning electron microscopy, and tensile tests. The flammability behaviors of filaments were evaluated using the oxygen index method. The effect of nanoparticles on structural properties and flame retardancy behaviors of filaments were summarized and discussed. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2085–2091, 2009

Key words: Nanocomposite; polypropylene; fiber; flame retardant

INTRODUCTION

Textile fibers are commonly used as apparel, upholstery, and carpets. Flame retardancy is an important and necessary property for some applications of these textile products such as curtains, floor coverings, and in some special areas. Furthermore since the late 1970s, in accordance with the rapid developments in science and technology the applications of textile fibers have also expanded to and increased, especially, in technical fields. Fibers are now widely used in the field of technical textiles such as military applications, safety and protective garments, automotive and aerospace applications, electronic and optical devices, geotechnical applications, and so on. These application areas require additional fiber properties and functions such as high mechanical performance, flame retardancy, chemical resistance, UV resistance, electrical conductivity, soil resistance, water repellency, magnetic field resistance, radar absorbing, etc. Therefore the number of studies on

modifying the properties of polymeric fibers by various ways has increased recently.

Using organic and inorganic particles as fillers in polymeric materials such as composites, films, and fibers is one of the methods of modifying these materials for high-technology applications. In addition to these attempts nanotechnology leads to developing the nanoscale systems and particles for various end uses such as nanocomposite fibers. As the size of particles decreases, their effects increase because of their larger total surface area per unit volume.^{1,2} Furthermore conventional methods used to modify fibers and fabrics do not, more often, lead to permanent effects and lose their functions after laundering or wearing, however because of their high surface energy nanoparticles present better affinity for fibers and fabrics and increase the durability of their function.³ Consequently, the number of studies about modifying the properties of polymeric textile fibers and fabrics by nanoparticles has increased recently.^{1,4–15}

In general two main methods are used to modify textile materials with nanoparticles; the first is that nanoparticles are incorporated in textile fibers and the second is that nanoparticles are treated on the textile materials during finishing processes. It can be expected that the nanoparticles could easily be incorporating in fibers. However, during the preparation, spinning, and drawing of fibers two main problems

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exist: These are the difficulty of obtaining homogeneous distribution of particles (particle aggregation) in the polymer and chemical compatibility (adhesion) of particles and polymers.^{2,8,9} Thus; appropriate way of mixing nanoparticles into the polymer is generally preferred. The three main ways of mixing nanoparticles into fiber-forming polymers are melt mixing, solution mixing, and *in situ* polymerization.^{2,9,16} There are also some other methods such as *in situ* sol-gel processing of particles inside the polymer and *in situ* formation of metal particles from suitable precursors for metal/polymer nanocomposites.² Among these methods direct mixing and especially melt mixing takes the advantages of traditional polymer processing techniques. It has already been demonstrated that well-established fiber processing technology can be successfully used for processing nanocomposite fibers.^{1,4-6,8-10,13} For this purpose nanoparticles and polymer are mixed with a twin screw extruder or blender before fiber spinning and drawing processes to produce nanocomposites (master batches). From another point of view, the dispersion of nanoparticles may be more homogeneous after modification of the interfaces (especially particles) and/or after solution mixing of nanoparticle/polymer before melt mixing and spinning.^{2,8,17,18} These attempts generally reduce particle agglomeration and increase particle-polymer compatibility. Solution mixing usually requires dissolving the polymer in an organic solvent and mixing with particles. This method, however, is not feasible for large-scale production of polymer nanocomposites.¹⁶

Polypropylene (PP) is one of the most widely used thermoplastic polymers for application in textile (especially in carpets and nonwovens) and plastics. This is attributed to its low density, low cost, easy processing, high-tensile strength and excellent chemical stability. However, it has some shortcomings such as low polarity, low dimensional, and thermal stability.^{1,16,19,20} PP burns very rapidly and has a high flammability because of its wholly aliphatic structure and rapid decomposition rate. Limit oxygen index (LOI) value of PP is about 18%.^{20,21} Therefore various attempts have been made to achieve flame retardancy of PP polymers and textiles.²⁰ Consequently, similar to other polymeric materials, the properties such as flame retardation, UV resistance, crystallization behavior, modulus, strength, hygienic behavior, and electrical resistance of PP composites, fibers, and films have been modified by compounding them with very small amounts of nanoparticles. Some examples of these attempts are observed in products like PP/silver,^{1,22} PP/carbon nanotubes,^{4,7,10} PP/carbon nanofiber,^{5,6,13} PP/SiO₂,^{8,9,17-19} PP/BaFe₂,²³⁻²⁵ PP/TiO₂.^{26,27} Although SiO₂ particles have already been used as fillers in

polymer compounds (such as composite materials), only a few papers^{8,9,18,28} have been published on characterization and in use properties of fibers or textiles modified with SiO₂ nanoparticles.

In this article, we have aimed to produce slow burning or flame retardant PP filaments for carpet pile yarns by compounding SiO₂ nanoparticles into polymer. Therefore, we present the preparation of PP filaments incorporating 0.3, 1, and 3% SiO₂ nanoparticles and investigate the effects of nanoparticles on the flame retardancy and structural behaviors of filaments. PP and SiO₂ nanoparticles were compounded before spinning. Filaments with trilobal cross sections were spun using pilot melt spinning equipment. The structural properties of composite fibers were analyzed using X-ray diffractometry, differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and tensile tests. Flame retardancy behaviors of filaments were investigated using oxygen index method. The effect of nanoparticles on flame retardancy behaviors and structural properties of filaments were also reported and discussed.

EXPERIMENTAL

Materials

SiO₂ spherical nanopowder (99.5%) was supplied from Aldrich. The average particle diameter of powder was 10 nm. Ecolen HZ21X, an isotactic PP (iPP) with a melt flow index of 35 g/10 min and density 0.90 g/cm³ was used for nanocomposite filament preparation.

Preparation of PP/SiO₂ nanocomposite filaments

The PP and SiO₂ nanoparticles were mixed by melt compounding using twin screw extruder before spinning. At first, PP chips were milled to a powder, then powdered PP and SiO₂ nanoparticles were dried in a vacuum oven. Prior to being fed to twin screw extruder the mixture of PP powder and SiO₂ nanoparticles was prepared, in which the content of SiO₂ nanoparticles were 0.3, 1, and 3%. The extrusion speed was 60 rpm and the temperatures in the six extrusion zones were 170-190-190-190-190-195°C, respectively. After a defined time of extrusion, the extruded material was cooled in a water bath, palletized, cut, and chips (master batch) of the above-mentioned concentrations were obtained. A control PP sample without SiO₂ nanoparticles was also subjected to the same process to obtain similar thermal history. PP-SiO₂ master batches (nanocomposites) were converted into filaments having trilobal cross section using pilot melt spinning machine (Emerson

and Renwick). Melt spinning was carried out on a single screw extruder with a spinneret containing 40 orifices. The extrusion speed was 15 rpm and the temperatures in the extrusion zones were 206–225–235–239–240 from feeder to spinneret, respectively. The as-spun filaments were subsequently drawn to a draw ratio of 2.5 at 115°C.

Measurements

To identify the SiO₂ particles dispersed in the PP filament digital images were obtained from fiber surfaces and cross sections using JEOL-6060 Scanning Electron Microscope (SEM). For SEM examinations, small pieces of fibers were cut and fixed to conductive adhesive tapes, then fiber samples were sputter coated with gold/platinum. The coated specimens were mounted on the microscope's stage and digital images were recorded.

The structure of nanocomposite fibers and control sample were analyzed using X-ray diffractometer (XRD) and differential scanning calorimeter (DSC). XRD studies were carried out with XRD Rigaku D/Max 2200 PC using Cu-K α radiation and operating at 40 kV and 36 mA. The diffraction angles (2θ) of each sample were measured from 3° to 90° at a scan speed of 4°/min. DSC measurements were performed at Perkin–Elmer/Pyris1 in N₂ at a heating and cooling rates of 20°C/min in the temperature range of 0–200°C. The melting temperature (T_m) and the crystallization temperature (T_c) of samples were obtained by this procedure. The percentage of the crystallinity of the samples was calculated as:

$$\text{Crystallinity(\%)} = \frac{\Delta H_f}{\Delta H_f^0} \quad (1)$$

where ΔH_f is the enthalpy of fusion of tested PP fiber samples calculated by dividing the endothermic peak area by the weight of PP within the nanocomposite fiber sample. ΔH_f^0 is the extrapolated value of enthalpy corresponding to melting of 100% crystalline PP which is obtained from literature as $\Delta H_f^0 = 165 \text{ J/g}$.²⁹

Tensile properties of fibers were measured using Instron-4411 tensile testing machine equipped with a 10N cell according to ASTM D-3822-07.³⁰ The gauge length was 20 mm and the crosshead speed was 20 mm/min. An average of 25 reading for each fiber sample was reported.

The combustibility of fiber samples were evaluated by LOI test, which measures the minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen that will just support flaming combustion. The oxygen index instrument, which was designed according to ASTM D-2863-76³¹ was used

for testing and tests were carried out using a modified sample holder for fibers.

RESULTS AND DISCUSSION

Surface observation

The longitudinal and cross-sectional micrographs of fibers determined from SEM records are given in Figures 1 and 2. Fiber surfaces were investigated with respect to their shape and uniformity. The neat fibers show a smooth surface along the length of fiber, but fibers filled with nano-SiO₂ particles show some surface irregularities as the content of nanoparticle increase. These surface protrusions of fibers are most probably due to nanoparticle agglomeration. It is also evident from the figures that the agglomerates are discontinuous throughout the fiber.

The cross sections of nanocomposite fibers also show the presence of fillers. The cross sections of the fibers are uniform and smooth for all applied concentrations. Consequently the surface SEM micrographs of the PP/SiO₂ nanocomposite fibers show number of irregularities throughout the fiber because of nanoparticle agglomeration. So that, as the content of particles increases, their distribution becomes nonhomogenous. But nevertheless, no inhomogeneities were observed in the cross-sectional images of fibers.

Structural analysis

Integrated X-ray diffraction profiles of produced fibers are given in Figure 3. The diffraction peaks of the PP crystals which range from 10° to 30° indicate a typical α form of PP crystals. In nanocomposite fibers, the diffraction pattern of PP crystals did not indicate any significant change. However, the degree of crystallinity (the intensity and height of peaks) changes slightly with respect to nanoparticle content. There is no significant change in the fibers filled with 0.3 and 1% nano-SiO₂, but in the case of fibers with 3% nano-SiO₂ lower crystallinity was observed. This phenomenon is probably because of the presence of large agglomerates.

Thermal properties

Crystallization and melting characteristics and DSC curves of fibers are presented in Table I and Figure 4, respectively. The shape of curves of both PP and PP/SiO₂ nanocomposite fibers are similar. Only minor differences could be observed in crystallization temperature (T_c) and in percentage crystallinity (X_c). The degree of crystallinity of PP enhanced by the addition of nano-SiO₂ was close to that of neat PP. The crystallinity increases slightly up to 56.2%

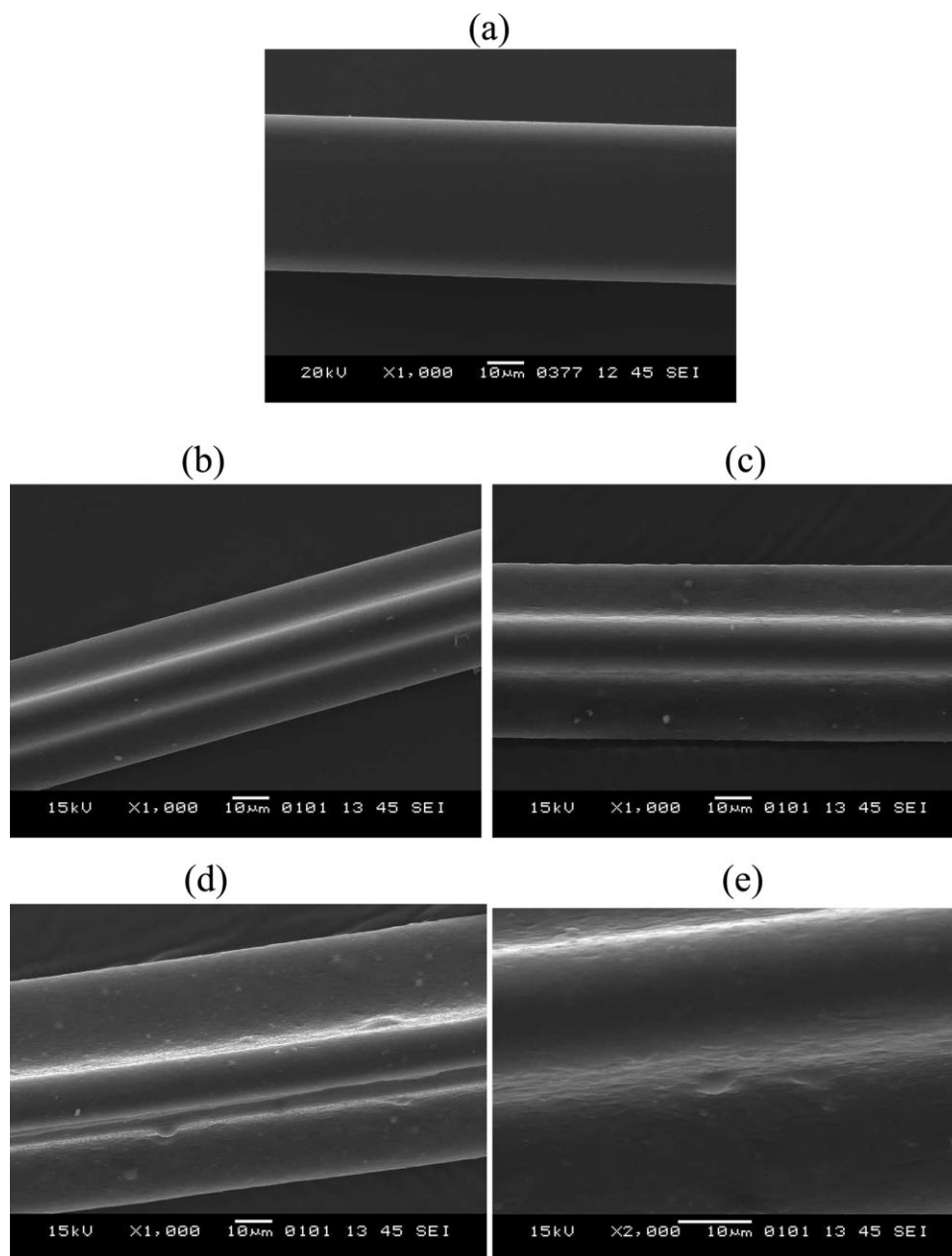


Figure 1 Longitudinal SEM images of nanocomposite fibers. (a) Neat PP, (b) 99.7% PP/0.3% nano-SiO₂, (c) 99% PP/1% nano-SiO₂, (d) and (e) 97% PP/3% nano-SiO₂.

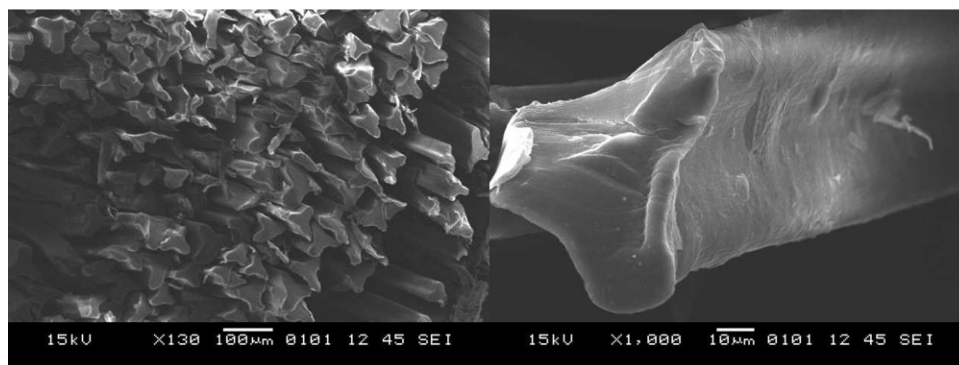


Figure 2 Cross-sectional SEM images of nanocomposite fibers.

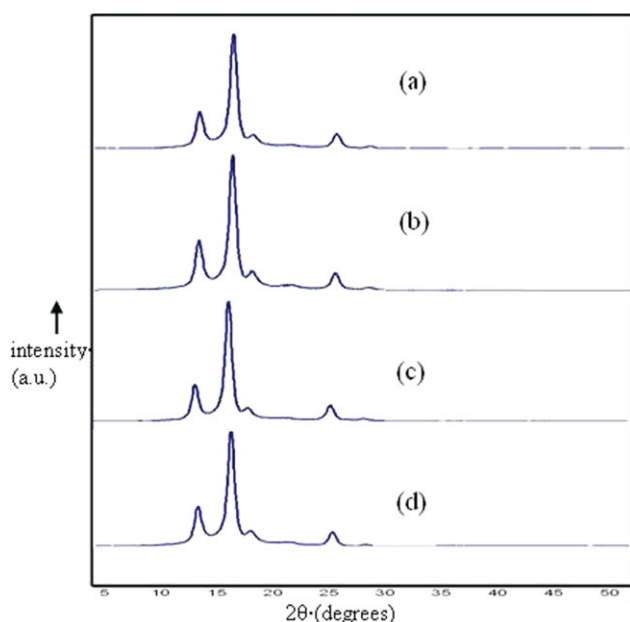


Figure 3 X-ray diffraction patterns of fibers. (a) Neat PP, (b) 99.7% PP/0.3% nano-SiO₂, (c) 99% PP/1% nano-SiO₂, and (d) 97%PP/3% nano-SiO₂. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

as the content of filler increases, however crystallinity decreases to 53.6% as the filler content increases up to 3%. These findings are most probably due to nucleation role of nano-SiO₂ in the crystallization of PP which results in a higher degree of crystallinity and higher crystallization temperature. But it can be inferred that larger aggregates prevent the crystal growth and hence reducing the crystallinity as the nano-SiO₂ content increases up to 3%. Since the addition of nanoparticles was not expected to affect the molecular weight or to cause any chain branching in PP, only the nucleating activity of the nanoparticles was considered in accordance with literature.¹⁸

Table I and Figure 4 show that the neat PP crystallized at 112.97°C, but crystallization temperature increased up to 116.49°C for nanocomposite fiber containing 3% SiO₂ particles. The increase of crystalline peak temperature was due to the increasing con-

TABLE I
Crystallization and Melting Characteristics of Fibers

Content of nano-SiO ₂ (%)	T_c (°C)	T_m (°C)	X_c (%)
0	112.97	164.29	53.4
0.3	113.82	166.51	55.5
1	115.80	168.48	56.2
3	116.49	165.88	53.6

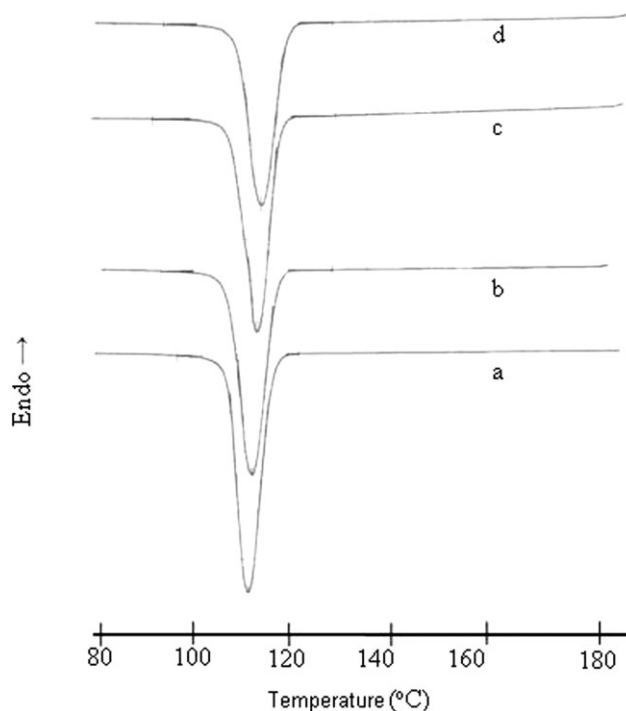


Figure 4 Crystallization curves of fibers. (a) neat PP, (b) 99.7% PP/0.3% nano-SiO₂, (c) 99% PP/1% nano-SiO₂, (d) 97%PP/3% nano-SiO₂.

tent of nano-SiO₂, but the melting temperature (T_m) remained somewhat unchangeable. This is a typical nucleating affect of nano-SiO₂ on PP cited in the literature.^{19,32}

Mechanical properties

Tensile properties of fibers such as strength and elongation were measured to evaluate the effect of nanoparticles on fiber properties. There were only small differences found. As seen in Table II, tensile strength of fiber decreases as the content of nano-SiO₂ particles increases, but at the content of 3% the strength jumps back to 2.58 g/denier. Since the fiber containing 3% nano-SiO₂ is more brittle than other fibers, it does not elongate much. Hence, more force requires for breaking it.⁷ Large aggregates of nano-SiO₂ particles in composite fibers did not seem to negatively affect the mechanical properties.

TABLE II
Mechanical Properties of Fibers

Content of nano-SiO ₂ (%)	Tensile strength (g/denier)	Elongation (%)
0	2.43	319
0.3	2.41	388
1	2.26	338
3	2.58	313

TABLE III
LOI of Fibers

Content of nano-SiO ₂ (%)	LOI (%)
0	18
0.3	20
1	21
3	22

Flame retardancy properties of the filaments

The PP burns very rapidly and has a high flammability due to its wholly aliphatic structure and rapid decomposition rate. One of the ways of producing flame retardant or slow burning PP is incorporating inorganic additives into polymer and several kinds of nanocompounds can be used to enhance the flame retardancy of polymer.²⁰ The oxygen index test was used to evaluate the flammability of fibers, because the test is a convenient method to obtain single numerical value of relative flammability of polymeric fibers.^{33,34} Since air comprises of about 20.95% oxygen by volume, any material with a LOI less than this value can burn easily in air. Conversely, a material with a LOI greater than 20.95% can reduce the flame after removal of the igniting source. On the other hand, several researchers have suggested that materials with a LOI greater than 28% are generally flame retardant and self extinguishing in oxygen index test,^{33,35} and materials between the thresholds 20.95% < LOI < 28% can be referred as slow burning materials in oxygen index test.³⁶ The result of combustibility of the samples containing nano-SiO₂ particles are presented in Table III.

The LOI of the neat PP filament is about 18% and the LOI of PP filament including 3% SiO₂ nanoparticle is 22%. It was obvious that the LOI of the fibers increased gradually with the increasing weight of nano-SiO₂ within PP fiber. Fibers containing 1 and 3% nano-SiO₂ particles reached the limits of slow burning materials. However, none of the composite fiber reached the requirement of fire-retardant threshold (LOI ≥ 28).

CONCLUSIONS

We prepared nanocomposite filaments from PP and nano-SiO₂ particles by melt blending using twin screw extruder and pilot spinning machine to obtain slow burning or flame retardant yarn for carpets. When we investigate the surface of fibers, some protrusions and nonhomogeneous dispersion of nanoparticles are observed. Nevertheless no inhomogeneities are observed in the cross-sectional images of fibers. From the X-ray diffraction peaks, typical α form of PP crystals are observed for all fibers. In nanocomposite fibers, the diffraction pattern of PP

crystals do not indicate any significant change. However degree of crystallinity changes ambiguously with respect to content of nano-SiO₂ particles because of the particle agglomerations. Besides, only minor differences could be observed from DSC curves. Crystalline peak temperature of fibers rises with the increasing content of nano-SiO₂ particles because of their nucleating effect. With regard to mechanical properties there are only small differences found. Fiber strength decreases as the content of nano-SiO₂ particles increases, but at the content of 3%, the strength jumps back to 2.58 g/denier. Flame retardancy (LOI) of filaments changes with the increasing weight of nano-SiO₂ particles. Filaments containing 1 and 3% nano-SiO₂ particles reach the limit values of slow burning materials in oxygen index test.

Consequently, the structural and mechanical properties of nanocomposite filaments including 0.3, 1, and 3% SiO₂ nanoparticle, have not changed significantly. However, the LOI of filaments have increased gradually in the presence of SiO₂ nanoparticles. For example, 3% nanoparticle addition provides 22% increase in LOI value of filaments. Thus, we can obtain slow burning filaments for carpet pile yarns containing 1 and 3% nano-SiO₂ using the process described earlier.

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